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WO 02/08309 A2

(54) Title: USE OF CROSS-LINKER AND COMPOSITIONS MADE THEREFROM

(57) Abstract: The invention provides a method of polymerizing or crosslinking cationically curable components using X-rays, gamma rays or electron beam as an energy source. As the initiator for the cationic polymerization, an onium gallate compound having an anion of the formula GaX_nR_b wherein X is a halogen atom or a hydroxy group, R is an aryl group or a substituted aryl group, a and b are each represent an integer of 0 to 4 provided that the sum of a and b is 4 is disclosed. The invention also provides a composite material and a method for preparing the composite material using an electron beam and the onium gallate compound as an initiator. Finally, disclosed is a photoresist material containing the onium gallate compound as the acid generator or crosslinking initiator.

USE OF CROSS-LINKER AND COMPOSITIONS MADE THEREFROM

5 The present invention relates use of a cross-linker and compositions made therefrom, in particular to use of an onium gallate initiator for polymerization and/or crosslinking of cationic active components via an electron beam, in composite and photoresist compositions.

10 Cationically curable systems which contain components that polymerize or crosslink in the presence of strong acids have been developed and improved over the last 15-20 years. Recent developments employ onium salts as initiators in these systems. These onium salts initiators generate strong acids upon exposure to an energy source, such as heat or electromagnetic radiation, e.g. actinic radiation, electron beam radiation, X-rays, gamma radiation, etc. The strong acids formed then cause the polymerization or crosslinking of cationically curable systems.

15 Electron beams (EB) have been used to polymerize and/or crosslink cationically curable components, among other uses. The electron beam uses high energy electrons from an accelerator to activate the decomposition of the onium salt initiator to form a strong acid, which initiates the polymerization and/or crosslinking of the cationically curable moieties.

20 Cationically polymerizable and/or crosslinkable systems have been used in fiber reinforced composites. Recently, attention has been given to using electron beams to crosslink resin matrices of composite materials. Using electron beams as the energy source for crosslinking the resin matrices of the composite material has advantages over thermal curing of the matrices. These advantages include, lower curing temperature, reduced curing times and improved handling, which result in improved product quality (improved physical properties) and lower production cost.

25 In addition, onium salt type initiators have been used as acid generators and crosslinking initiators for photoresist compositions used to form photo images and relief images. In forming such images, a composition containing a resin material is either crosslinked in the presence of an acid (so-called negative resist) or are degraded in the presence of an acid (so-called positive resist). Some onium salt type initiators are known to generate acids upon exposure to an energy source such as heat and photo-energy, e.g. UV radiation, electron beams, gamma

radiation, etc. In both types of photoresist systems, a resin component must be present in the photoresist composition which contains moieties that render the resin soluble in an aqueous alkaline solution. The aqueous alkaline solution is used to develop the resist material, thereby forming the image.

5 Based on investigations carried out by the inventors of the present application, a new class of onium salt initiators has been discovered and these onium salts are effective for the cationic polymerization or crosslinking of an acid curable component. It has further been discovered that the onium salts used in the present
10 invention are also effective as curing initiators and acid generators for negative and positive photoresist compositions, respectively.

The onium salt initiator used in the methods and compositions of the present invention contains conventional onium salt cations. The new feature of the onium
15 salts used in the methods and compositions of the present invention is the anion of the salt. The anion has the formula $GaX_aR_b^-$, wherein X is a halogen atom or a hydroxy group, R is an aryl group or substituted aryl group, a and b are each represent an integer of 0 to 4, provided that the sum of a and b is 4. The onium salt initiator of the present invention is referred to as an "onium gallate".

20 DE 4024661 (Wewers et al) describes salts which are useful as initiators for polymerization of epoxy or vinyl groups. Optionally certain anions of these salts comprise gallium amongst many other possible elements. However these anions all comprise aliphatic " $-CF_3SO_3^-$ " groups and an anionic group such as Cl^- or SO_3^-
25 to bear the negative charge.

EP 0442635 (=US 5084586 & US 5124417) (3M) also describe various salts which are useful as initiators for cationic polymerization and may comprise anions containing a gallium atom (again as an option from many other elements).
30 However in these anions the gallium atom is always substituted directly with a " $-SO_3^-$ " group.

Thus the above prior art anions have a very different structure to those gallate anions described herein and used in the present invention. The onium gallates
35 used in the methods and compositions of the present invention are described in the co-pending application WO 01/12720 (= US 6,166,233) of priority date August 17, 1999, which is hereby incorporated by reference.

- The first aspect of the present invention relates to a method of using actinic radiation, an electron beam (EB), X-Ray and/or gamma radiation to polymerize or crosslink a cationic polymerizable or crosslinkable component(s). It has been discovered that a composition containing a component which is capable of cationic polymerizing or cationic crosslinking and an onium salt having the anion described above can very effectively be polymerized or crosslinked using actinic radiation, X-rays, gamma rays and/or an electron beam to give compositions having improved properties. An electron beam is preferred.
- 10 A second aspect of the present invention is a composite formed by curing a cationically curable resin using the process of the first aspect. The composites contain reinforcing materials, such as fibers, in addition to the cationic active component and onium gallate initiator.
- 15 A third aspect of the present invention provides a photoresist material and a method for forming a photoresist relief image. In this aspect of the present invention, conventional resin materials used in photoresist materials, both negative and positive, are blended with the onium gallate. Further, the present invention also provided for a method of forming a photoresist relief image on a substrate by exposing the photo resist material to an energy source, followed by developing the exposed composition.
- 20

Other aspects of the present invention are given in the claims.

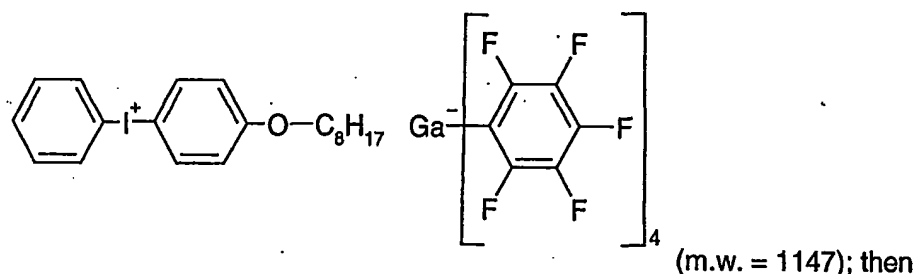
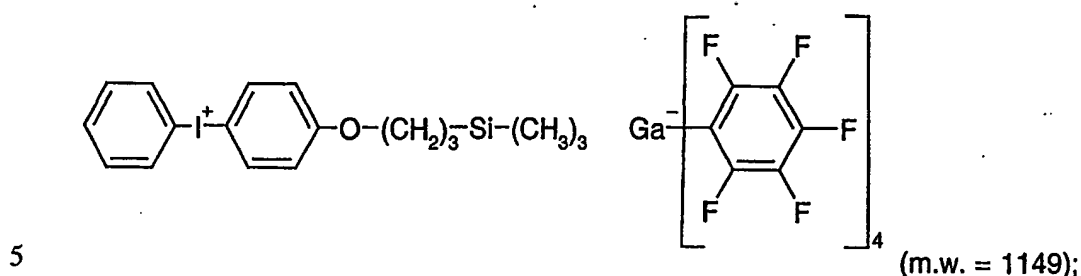
- 25 Therefore broadly in accordance with the present invention there is provided; a process for polymerizing or cross-linking a cationic polymerizable or cross-linkable component, said process comprising:
- a) forming a composition containing a component which is capable of cationic polymerizing or cationic cross-linking and an onium salt having an anion of the
- 30 formula GaX_aR_b , wherein X is a halogen atom or a hydroxy group, R is an aryl group or a substituted aryl group, a and b are each represent an integer of 0 to 4 provided that the sum of a and b is 4; and
- b) exposing the composition to radiation selected from the group consisting of actinic radiation, X-rays, gamma-rays and and/or an electron beam.

35

In the process of the present invention a preferred proviso is when:

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the polymerizable component is a matrix of the diglycidyl ether of bisphenol-A available commercially from Dow Chemical under the trademark DER 332; and the onium salt is present in an amount of 1% by weight of the composition and is either:



the radiation used in step (b) is other than an electron beam at a beam voltage of 200mV and a dose of 10 Mrad.

10

Preferably the composition obtained and/or obtainable by the process of the invention has at least one of the following properties:

- i) a flexural modulus of less than about 2.5 Gpa, more preferably from about 2.0 to about 2.5 Gpa;
- 15 ii) a service temperature of greater than about 150°C, more preferably from about 150°C to about 160°C;
- iii) a T_g (measured in a conventional manner as a function of the loss modulus) of greater than about 180°C, more preferably from about 180°C to about 195°C; and/or
- 20 iv) a T_g (measured in a conventional manner as a function of the peak in a tan delta plot) of greater than about 207°C, more preferably from about 207°C to about 212°C.

25 The onium gallates used in the methods and compositions of the present invention are preferably those described in WO 01/12720. These onium gallates include a

cationic moiety and an anionic gallate moiety. The cationic moiety can be any cation of onium salts such as diaryl iodonium, iodonium, pyrylium, thiapyrylium, sulfonium, phosphonium, ferrocenium or diazonium ions. The preferred cation ions are diaryl iodonium cations or triaryl sulfonium cations.

5

The anionic gallate has the general formula GaX_aR_b^- , wherein X is a halogen atom or a hydroxy group, R is an aryl group or a substituted aryl group, a and b each represent an integer of 0 to 4, provided that the sum of a and b is 4. The aryl groups representing R can be the same or different and may be aryl groups having an electron withdrawing capacity. Examples of such aryl groups include, but are not limited to, phenyl groups, phenyl groups substituted by at least one electron-withdrawing group, such as halogen atoms, CF_3 , NO_2 , CN and the like; or is an aryl radical containing at least two aromatic ring members, such as biphenyl, naphthyl and the like, which are optionally substituted by electron withdrawing groups such as halogen atoms, CF_3 , NO_2 , CN and the like. Preferably, the aryl groups are substituted with the electron withdrawing groups defined above. The preferred electron withdrawing groups are halogen atoms, most preferably, fluorine atoms.

The gallate anions which can be used in the methods and compositions of the present invention include, but are not limited to, $[\text{Ga}(\text{C}_6\text{F}_5)_4]^-$, $[\text{Ga}(\text{C}_6\text{H}_4\text{CF}_3)_4]^-$, $[(\text{C}_6\text{F}_5)_2\text{GaF}_2]^-$, $[(\text{C}_6\text{F}_5)\text{GaF}_3]^-$, and $[\text{Ga}(\text{C}_6\text{H}_3\text{F}_2)_4]^-$.

Representative onium cations are well known to those skilled in the art and are described in detail in, for example, U.S. Patents 5,550,265, and 5,340,898 to Rhone-Poulenc Chimie and U.S. Patent 5,639,802 to Spectra Group Limited and include iodonium, pyrylium, thiapyrylium, sulphonium, phosphonium, ferrocenium, and diazonium ions. Preferred cations are, for example, arylodonium ions such as 4-octyloxyphenylphenyl iodonium (OPPI), 4,4'-dimethyldiphenyliodonium, 4-(3-trimethylsilylpropyloxy)phenylphenyl iodonium and diphenyliodonium: sulphonium ions include triarylsulphonium ions such as triphenyl sulphonium ion and 4-octyloxyphenyl sulphonium ion. Particularly preferred is the cation OPPI, which tends to be more soluble in epoxy resins than other cations. However, other onium cations are known to those skilled in the art and can be used in the process and compositions of this invention.

35

The onium salts used in the methods and compositions of the present invention can be prepared by known methods, such as an exchange reaction between a salt of the cationic moiety and an alkali metal salt of the anionic moiety. Examples of

salts of the cationic moiety include, but are not limited to, halides such as chloride, iodide, etc. and other salts such as hexafluorophosphate, tetrafluoroborate, tosylate and others. Alkali metal salts and alkaline earth metal salts of the anionic moiety include salts such as sodium, lithium, potassium and magnesium salts.

- 5 The reaction conditions, including the respective amounts of the reactants, particular solvents, temperature and other reaction parameters can be easily determined by those skilled in the art. The methods used must permit recovery of the desired initiator salt in the solid state, by filtration of a precipitate formed or in an oily state by extraction using a suitable solvent.

10

The salts of the anionic moiety can be prepared by methods known to those skilled in the art. An example of a method which can be used is an exchange reaction between a halogallate compound and an organometallic compound. The metal atom in the organometallic compound can be, for example, magnesium, lithium, tin, cadmium, copper, zinc and other metals. The organic part of organometallic compound should contain the desired organic groups in a stoichiometric amount. Optionally, the product of the exchange reaction can be further treated in a hydrolysis reaction using an aqueous solution of an alkali metal halide. The synthesis described above is analogous to the synthesis described in J. Organometallic Chemistry, vol. 178, p. 1-4, (1979); J.A.S.C., 82, 5298 (1960); Anal. Chem. Acta, 44, 175-183 (1969); U.S. Patent No. 4,139,681, hereby incorporated by reference, and Zh. Org. Khim., vol 25, No 5, pages 1099-1102, (May 1989).

15

20

- 25 Onium salts used to prepare the onium gallates used in the process and compositions of the present invention can be prepared by methods well known to those skilled in the art, including those methods described in U.S. Patents 5,550,265, 5,340,898, and 5,639,802, each hereby incorporated by reference.

30

In the method of the first aspect of the present invention, any component which can be polymerized or crosslinked via a cationic polymerization or crosslinking can be used. Examples of the components which can be polymerized or crosslinked via cationic polymerization or crosslinking are monomers, oligomers and polymers having one or more cationically curable functional groups. Examples of cationically curable functional groups include, but are not limited to, epoxy groups, vinyl or allyl groups, vinyl ether groups, allyl ether groups, styrenic groups and styryloxy groups, cyclic ether containing groups including oxetane groups and others, cyclic ester containing groups, cyclic sulfide groups, melamine formaldehyde containing

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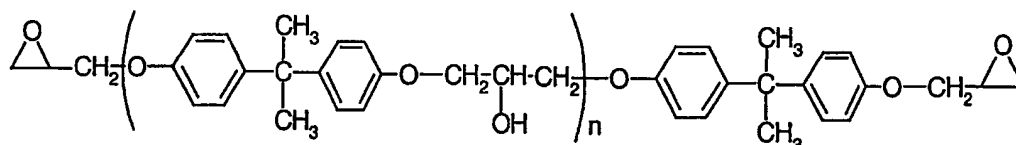
groups, phenolic formaldehyde groups, cyclic organosiloxane containing groups, lactone containing groups, lactam containing groups, and cyclic acetal containing groups.

- 5 The composition may also include additives, including reactive and non-reactive diluents, polyols, phenolic materials, toughening agents, and fillers such as silica, alumina, and titanium containing materials.

10 Particularly preferred cationic polymerizable or crosslinkable components used in the present invention are epoxy containing monomers, oligomers and polymers; vinyl ether containing monomers, oligomers, and polymers; and cyclic ether containing monomer, oligomers and polymers.

15 In particular, the epoxy resin can include those from any of the following glycidyl ethers:

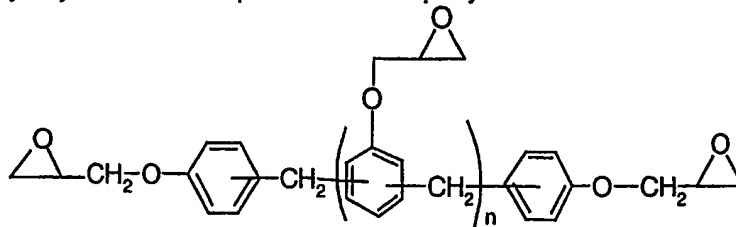
1 Diglycidyl ethers of Bisphenol A of the formula:



where $n=0$ to 10.

20 These resins are available from a number of manufacturers such as Shell Chemical Company, DOW Chemical Company, and Ciba Specialty Chemicals Corporation in a variety of molecular weights and viscosities. Examples include: DER 332, DER 330, DER 331, DER. 383 (DOW trademarks); Epon 825, Epon 826, and Epon 828 (Shell trademarks); and Tactix 123, Tactix 138, and Tactix 177, 25 Araldite GY 6008, Araldite GY 6010, and Araldite GY 2600 (Ciba Specialty Chemicals Corporation trademarks).

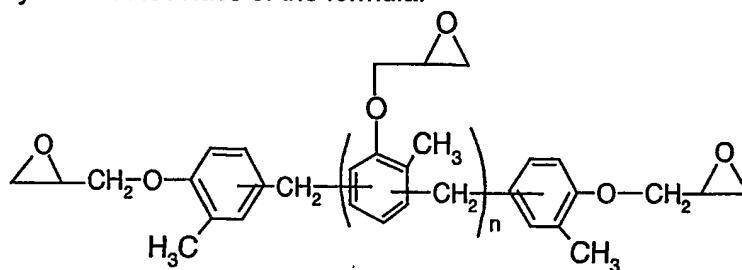
2A Diglycidyl ethers of Bisphenol F and Epoxy Phenol Novolacs of the formula:



Diglycidyl ethers of Bisphenol F, when $n=0$, or Epoxy Phenol Novolacs, when $n>0$.

These materials are available from a number of different manufacturers in a variety of molecular weights and viscosities. Examples include: Epon 155, Epon 160, Epon 861 and Epon 862 (Shell trademarks), DEN 431, DEN 436, DEN 438, DEN 439, DEN 444, and Tactix 785 (Dow trademarks), Araldite PY 306, Araldite EPN 1138, Araldite EPN 1139, Araldite EPN 1179, Araldite EPN 1180, Araldite EPN 9880, Araldite GY 281, Araldite GY 282, Araldite GY 285, Araldite GY 308, Araldite LY 9703, Araldite PY 307, and Araldite XD 4995, and Tactix 785 (Ciba Specialty Chemicals Corporation trademarks), and Epalloy 8230, Epalloy 8240, Epalloy 8250, Epalloy 8330, and Epalloy 8350 (CVC Specialty Chemicals trademarks).

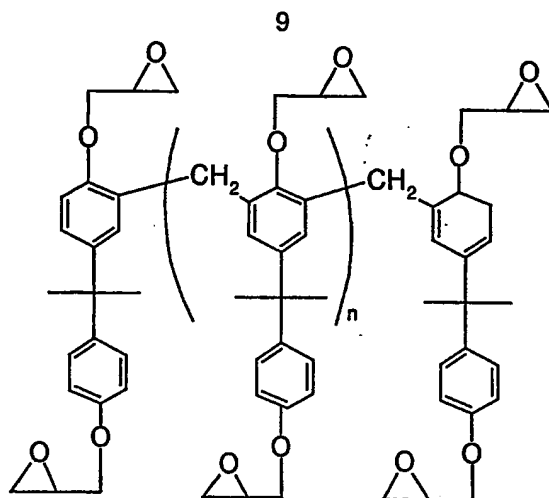
2B Epoxy Cresol Novolacs of the formula:



15 where $n>0$ can be used.

Epoxy Cresol Novolacs are available from a number of different manufacturers in a variety of molecular weights and viscosities. Examples include: Epon 164 and Epon RSS-2350 (Shell trademarks), and Araldite ECN 1235, Araldite ECN 1273, Araldite ECN 1280, Araldite ECN 1282, Araldite ECN 1299, Araldite ECN 1400, Araldite ECN 1871, Araldite ECN 1873, Araldite ECN 9511 and Araldite ECN 9699 (Ciba Specialty Chemicals Corporation trademarks).

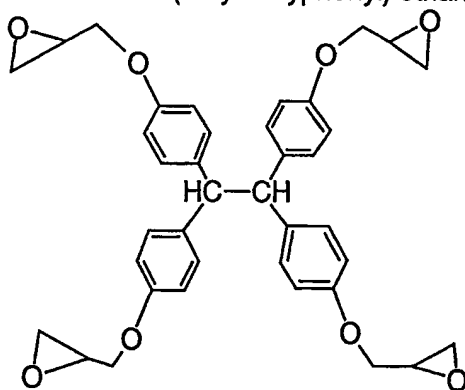
2C. Bisphenol A Epoxy Novolacs of the formula:



where $n=0$ to about 2 or more.

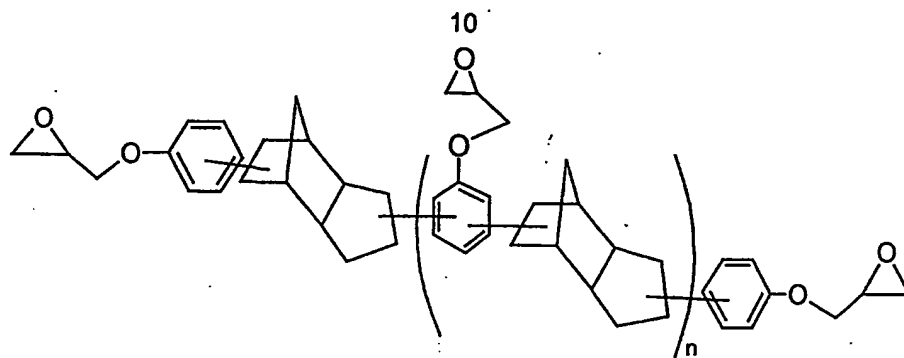
Bisphenol A epoxy novolacs are commercially available in a variety of molecular weights and viscosities as the SU series of resins (Shell Chemical trademark).

3. Tetraglycidyl ether of tetrakis (4-hydroxyphenyl) ethane of the formula:



This is commercially available as Epon 1031 (Shell Chemical trademark) and Araldite MT 0163 (Ciba Specialty Chemicals Corporation trademark).

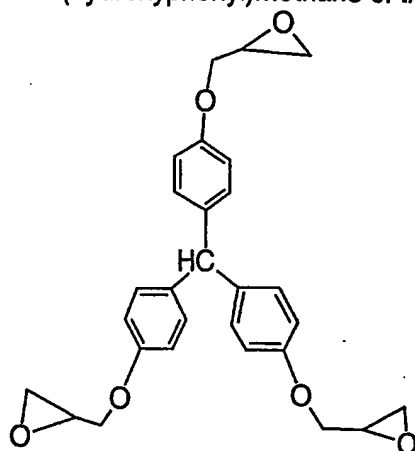
4. Glycidyl ethers of the condensation product of dicyclopentadiene and phenol of the formula:



This product is commercially available as Tactix 556 (Ciba Specialty Chemicals Corporation trademark) where n is approximately 0.2.

5

5. Triglycidyl ether of tris(hydroxyphenyl)methane of the formula:

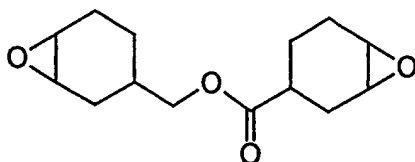


This product is available as Tactix 742 (Ciba Specialty Chemicals Corporation trademark).

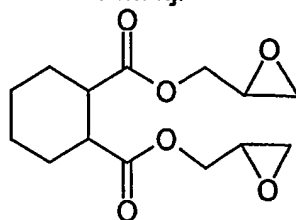
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The forgoing epoxy materials can be used alone or as mixtures of several of the materials.

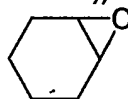
15 The epoxy resin used in the process of the present invention may also contain the following cycloaliphatic epoxides of the indicated formulas, either as the main ingredient of the binder formulation or as a diluent:



- 3',4'-epoxycyclohexylmethyl 3,4-epoxycyclohexanecarboxylate
 [available as ERL-4221, Cyacure UVR-6110 and UVR 6105 (Union Carbide Corporation trademarks), Araldite CY-179 (Ciba Specialty Chemicals Corporation trademark), Uvacure 1500 (UCB Chemicals trademark) and as Celloxide 2021
 5 (Daicel Chemical Industries Ltd. trademark)].

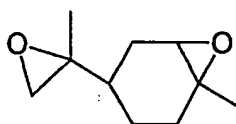


Diglycidyl ester of hexahydrophthalic anhydride (available as CY 184 Ciba Specialty Chemicals Corporation trademark)).

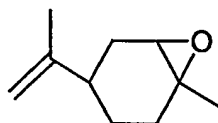


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Cyclohexane oxide.

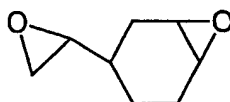


Limonene diepoxide (available as Celloxide 3000 (Daicel Chemical Industries Ltd. trademark)).



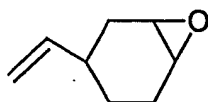
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Limonene monoxide



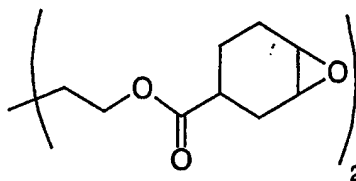
Vinyl cyclohexene dioxide (available as ERL-4206 (Union Carbide Corporation trademark)).

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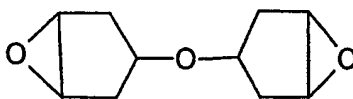


Vinyl cyclohexene oxide (available as Celloxide 2000 (Daicel Chemical Industries Ltd. trademark)).

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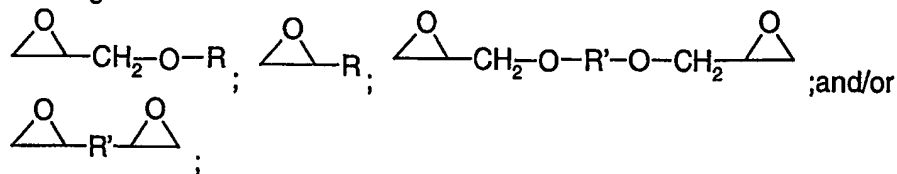
Bis (3,4-epoxycyclohexylmethyl) adipate



Bis (2,3-epoxy cyclopentyl) ether

Other epoxy resins or monomers which can be used in the EB process aspect of the present invention include 2-(3,4-Epoxycyclohexyl 5,5-spiro-3,4-epoxy) cyclohexane-metadioxane (available as ERL-4234 (Union Carbide Corporation trademark)), epoxycyclohexanecarboxylate modified β -caprolactone (available in various molecular weights as Celoxide 2081, Celoxide 2083, and Celoxide 2085 (Daicel Chemical Industries Ltd. trademarks)), (3,4-Epoxy cyclohexyl) methyl acrylate (available as Cyclomer A-200 (Daicel Chemical Industries Ltd. trademark)), and (3,4-Epoxy cyclohexyl) methyl methacrylate (available as Cyclomer M-100 (Daicel Chemical Industries Ltd. trademark)). These materials can also be used alone or as mixtures.

The epoxy resins can also include polymers with pendent epoxy or cycloaliphatic epoxide groups. The epoxy resin may also include those from the epoxides of the following structures:



wherein R is a monovalent radical, which include a linear, cyclic or branched alkyl group having up to about 18 carbon atoms, e.g., butyl, heptyl, octyl, 2-ethyl hexyl or cyclohexyl; an aryl group e.g., phenyl or alkyl-phenyl such as, for example, cresyl, t-butyl phenyl and nonylphenyl; and an alkenyl group such as allyl. R' is a bivalent radical which include linear or branched alkylene groups having up to about 18 carbon atoms, oxyalkylene groups having, for example, the following

formulae $(\text{CH}_2\text{CH}_2\text{O})_n (\text{CH}_2\text{CH}_2\text{CH}_2\text{O})_n$ and the like, where n may be, for example, 1 to about 10.

5 These materials are commonly used, and commercially available epoxy reactive diluents and functional modifiers. Specific examples of these materials may be found in Handbook of Composites, Edited by George Lubin, Van Nostrand Reinhold Company, Inc., New York, N.Y. (1982), pages 61 to 63, and Shell Chemical Company technical brochure SC-1928-95, HELOXY[®] Epoxy Functional Modifiers.

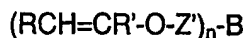
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Certain of the epoxy materials are either high viscosity liquids or solids at room temperatures. Therefore, it is contemplated that the higher viscosity materials may be blended with lower viscosity epoxy materials or with reactive or non-reactive diluents in order to achieve the desired viscosity for ease in handling and processing. Heating may be required to achieve the desired flow properties of the uncured formulation but temperatures should not be sufficiently high to cause thermal curing of the epoxy group. Specific blends have been found to have a good overall combination of low viscosity in the uncured states and high glass transition temperature, flexural strength and modulus when cured. One blend which can be mentioned is a high performance semi-solid epoxy such as Tactix 556 with lower viscosity bisphenol A or bisphenol F based glycidyl ether epoxies such as Tactix 123 or Epon 861, respectively.

15

Examples of suitable monomers, oligomers and polymers having at least one or more vinyl ether groups include those of the following general formula:

20



where

n is an integer from 1 to 4

25

R and R' are each, independently H or C_{1-8} alkyl,

Z' is a direct bond or a divalent moiety having 1-20 carbon atoms selected from the group consisting of alkylene, cycloalkylene, or polyalkylene ether moieties; and

B is hydrogen or a moiety derived from aromatic and aliphatic hydrocarbons, alcohols, cycloaliphatic hydrocarbons, esters, ethers, siloxanes, urethanes, and carbonates, each containing from 1 to 40 carbon atoms.

30

Examples of vinyl ethers usable in the process of the first aspect of the present invention are generally defined by the following formulae:

a) Vinyl ether terminated aliphatic monomers of the formula



5 where

n is 1 to 4,

m is 0 to 5,

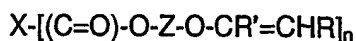
M is a mono, di, tri, or tetra functional aliphatic or cycloaliphatic moiety having from 1-40 carbon atoms;

10 Z is a divalent moiety having 1-20 carbon atoms selected from the group consisting of alkylene, cycloalkylene or polyalkylene moieties; and

R and R' are each, independently, H or C₁₋₈ alkyl.

b) Vinyl ether terminated ester monomers of the formula

15



where

n is 1 to 4,

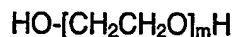
20 X is a mono, di, tri, or tetra functional moiety having from 1-18 carbon atoms selected from the group consisting of alkylene, arylene, aralkylene and cycloalkylene moieties,

Z is a divalent moiety having 1-20 carbon atoms selected from the group consisting of alkylene, cycloalkylene, or polyalkylene ether moieties, and

25 R and R' are each, independently, a monovalent moiety selected from the group consisting of H and alkyl groups having 1-8 carbon atoms.

c) Vinyl ether terminated ether monomers derived from ether compounds such as

30



wherein

m is 2 to 5.

d) Vinyl ether terminated aromatic monomers of the formula

35



where n is 1 to 4,

15

Y is a mono, di, tri, or tetrafunctional aromatic moiety having 6 to 40 carbon atoms;
and

Z, R' and R" are as defined above.

- 5 e) Vinyl ether terminated siloxane monomers of the formula:

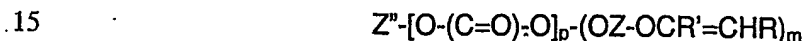


where

n is 1 to 4

- 10 A is a polysiloxane with from 2 to 50 silicon atoms; and
R, R' and Z' are as defined above.

- f) Vinyl ether terminated carbonate monomers of the formula:



where

m is 1 to 4,

Z'' is a diester, diol or polyol moiety of from 2 to 20 carbon atoms,

p is 0 to 3, and

- 20 R, R' and Z are as defined above.

Common vinyl ether monomers, oligomers and polymers which are suitable in the process of the present invention include ethyl vinyl ether, propyl vinyl ether, isobutyl vinyl ether, octadecyl vinyl ether, hydroxybutyl vinyl ether, propenyl ether
25 of propylene carbonate, dodecyl vinyl ether, cyclohexyl vinyl ether, 2-ethylhexyl vinyl ether, butyl vinyl ether, ethyleneglycol monovinyl ether, diethyleneglycol divinyl ether, butanediol monovinyl ether, butane diol divinyl ether, hexane diol divinyl ether, ethylene glycol butyl vinyl ether, triethylene glycol methyl vinyl ether, cyclohexane dimethanol monovinyl ether, cyclohexane dimethanol divinyl ether, 2-
30 ethylhexyl vinyl ether, poly-THF divinyl ether, $CRH=CR-[O(CH_2)_4-O]_n-CR=CRH$, pluriol-E-200-vinyl ether, $CRH=CR-[O-CH_2-CH_2]_n-O-CR=CRH$, bisphenol A divinylether and the like.

Examples of cyclic ethers which can be used in the present invention include
35 butylene oxide (oxetane), pentylene oxide, 1,3,5 oxanes and oligomers or polymers having related functional groups.

- Reactive diluents may be optionally be employed in the formulations to be cured by the new initiator in an amount of up to about 50 % by weight of the formulation. These include low viscosity epoxides or diepoxides, oxetanes or dioxetanes, low viscosity alcohols, polyols, and/or phenols, vinyl ethers, vinyl monomers, cyclic ethers such as tetrahydrofuran, cyclic carbonates and esters, acrylates and methacrylates, and compounds containing more than one type of reactive functionality in the same molecule.
- 5
- Solvents may be added to the formulation to adjust the viscosity of the uncured formulation to that desired for application. Generally, but not always, solvents would be removed by evaporation from the applied formulation prior to curing. Solvents can be employed in amounts up to about 90 % by weight of the curable formulation.
- 10
- Alcohols (0 to about 20 % by weight), polyols (0 to about 50 % by weight) and phenolic compounds (0 to about 50 % by weight) may be added to the formulation to modify the uncured rheology or to improve the cured properties of the subject formulations.
- 15
- Reactive and non-reactive toughening agents may optionally be employed in an amount of up to about 50 % by weight of the formulation. These agents are used to increase the impact resistance and modulus of the systems to which they are added.
- 20
- Reactive toughening agents include materials which have functionality which will react under acid catalyzed conditions such as epoxy and/or hydroxy terminated rubbers.
- 25
- Non-reactive toughening agents include materials which do not have functionality which will react under acid catalyzed conditions, or which will react poorly under such conditions, such as polybutadienes, polyethersulfones, polyetherimides, acrylics, and the like.
- 30
- Mineral fillers may be added. Such fillers are employed in amounts of up to about 70 % by weight of the formulation. Fillers include calcium carbonate (at some expense of cure speed), alumina oxide, amorphous silica, fumed silica, sodium aluminum silicate, titania oxide, clay, etc. Fillers may be surface treated to increase filling ability, or to enhance adhesion to the epoxy resin or to other
- 35

components of the abrasive binder, and/or to improved properties of the cured resin. Nanoparticle fillers of various types may also be employed.

5 Pigments or dyes can also be added to the formulation to achieve a desired color or hue. Such materials may be those which are conventionally employed in the art and are used in amounts of up to about 10 % by weight of the formulation.

10 The polymerizable and/or crosslinkable compositions used in the EB polymerization or crosslinking of the present invention are polymerized or crosslinked by exposing the composition to an electron beam. The typical exposure dose is between 0.1 and 500 kGy. Preferably, the dose is generally between 0.8 and 200 kGy, and most preferably between 50 and 150 kGy. Using less than 0.1 kGy will generally not result in any significant polymerization or crosslinking of the cationic active component. Using more than 500 kGy may result in the degradation of the product formed. It is noted, however, that the exact dose needed to cure a given material will vary and depends on factors such as the particular material being polymerized or crosslinked. Any electron beam generating device can be used, however, factors should be taken into account such as the thickness of the resulting product and the materials used to produce the resulting product. The electron beam generating device should be selected so that it has sufficient power to polymerize or crosslink the material.

25 The cationic active components described above have been previously used in composite materials. A composite material is one which contains a fiber reinforcement material such as, for example, carbon fibers, aramid fibers and glass fibers, which is dispersed within the cationic active component matrix. These reinforcement materials are commercially available. In addition, composites can also be made by impregnating a mat of the fiber material with the resin material. Composites have been used in a wide variety of applications, particularly in applications where materials that are light weight and have a high strength are needed. Examples include aerospace, transportation, sporting goods and infrastructure applications.

35 Conventional methods known to those skilled in the art can be used to fabricate the composites of the present invention. Examples of such methods include filament/tape winding, resin transfer molding, pultrusion and hand lay-up, as well as other known methods. Preferably, the curable matrix is an epoxy resin material,

a vinyl ether containing resin or an oxetane containing resin, such as those resin components described above.

5 In curing the resin material used in the composite, care must be taken to ensure that the resin is cured. Electron beam irradiation to cure composite materials can be used so long as the thickness of the composite material is not too thick. This is because the electron beam can only penetrate a certain distance into the composite material. The penetration distance is a function of the electron beam energy and the density of the composite material. However, it is noted that
10 methods are known to those skilled in the art to overcome the limits of the electron beam, including exposing two sides of the composite material to be cured to the electron beam and using a higher energy electron beam.

15 Photoresist materials typically comprise a resin binder and a photoactive component. In the photoresist materials of the present invention, the photoactive component is the onium gallate compounds described above. For a resin binder to be useful in a photoresist, the binder must typically contain polar groups which impart aqueous alkaline developability to the photoresist composition and the resin must be present in the material in an amount to render the resist material
20 developable with an aqueous alkaline solution. Examples of the polar groups include hydroxy or carboxylate groups.

Any resin used in conventional photoresist materials can be used in the present invention. Preferred resins include phenolic resins. The phenolic resins which can
25 be used in the photoresist of the present invention are known to those skilled in the art and include, for example, phenol aldehyde condensates, poly(vinylphenols), copolymers of phenol and nonaromatic cyclic alcohol units, bis-hydroxymethylated compounds and block novolak resins. Such resins are described in U.S. Patent 5,731,364, which is hereby incorporated by reference.

30 In positive photoresist compositions, the resin material contains a group which is acid labile either in a side chain or in the resin backbone. Examples of acid labile groups include acetate groups, such as t-butyl acetate, oxycarbonyl groups, such as t-butyl oxycarbonyl (t-Boc), acetals and ketals. These groups, in the presence
35 of the acid generated by exposing the onium gallate photoinitiator of the present invention to an energy source, e.g., UV radiation, electron beams, gamma radiation, etc., are converted back to the hydroxy groups. The presence of the hydroxy groups in the exposed portion of the resin render the resin material soluble

in an aqueous alkaline solution. This allows the exposed portion of the resin to be removed from the substrate to which it is applied. The portion of the resin which is not exposed to the energy source is not soluble in the alkaline solution due to the presence of the acid labile groups remaining intact on the resin.

5

In a negative resist material, an additional component is present in the resist composition. The additional component is a crosslinking agent which reacts with the soluble functional groups of the resin to be reacted. Therefore, the exposed portion of the photoresist material is not soluble in the alkaline developing solution and the unexposed portion of the resin is soluble in the alkaline developing solution.

10

Examples of crosslinking agents useable in negative photoresist material include amine- based material such as melamine, benzoguanamine based materials and urea based materials. Other crosslinking agents known to those skilled in the art can also be used.

15

Photoresist relief images are formed on substrates by applying the photoresist material to the substrate, followed by exposing the photoresist coating to a patterned activating radiation and developing the exposed photoresist layer to provide a relief image. The photoresist film may be applied to the substrate using any conventional methods known to those skilled in the art including liquid coating and dry film coating. The substrates which can be provided with a relief image include microelectronic wafers, such as silicon, silicon dioxide and others conventionally used in the microelectronic industry; and flat panel display substrates such as flat panel liquid crystal displays.

20

25

Broadly the present invention comprises a process for polymerizing or crosslinking a cationic polymerizable or crosslinkable component, said process comprising: forming a composition containing a component which is capable of cationic polymerizing or cationic crosslinking and an onium salt having an anion of the formula GaX_aR_b wherein X is a halogen atom or a hydroxy group, R is an aryl group or a substituted aryl group, a and b are each represent an integer of 0 to 4 provided that the sum of a and b is 4; and exposing the composition to an electron beam.

30

35

The onium salts may contains a cation selected from the group consisting of iodonium, pyrylium, thiapyrylium, sulphonium, phosphonium, ferrocenium, and diazonium ions,

- 5 Preferably the cation is an iodonium cation, more preferably a diaryliodonium cation, most preferably 4-octyloxyphenylphenyl iodonium.

Preferably the cation is a sulfonium cation, more preferably a triaryl sulfonium cation; most preferably a dialkylphenylacyl sulfonium cation.

10

Preferably the anion is selected from the group consisting of $[\text{Ga}(\text{C}_6\text{F}_5)_4]^-$, $[\text{Ga}(\text{C}_6\text{H}_4\text{CF}_3)_4]^-$, $[(\text{C}_6\text{F}_5)_2\text{GaF}_2]^-$, $[(\text{C}_6\text{F}_5)\text{GaF}_3]^-$ and $[\text{Ga}(\text{C}_6\text{H}_3\text{F}_2)_4]^-$; more preferably is $\text{Ga}(\text{C}_6\text{F}_5)_4]^-$.

- 15 Preferably in the process of the present invention, the composition is exposed to a radiation dose between about 0.8 to about 200 kGy, more preferably from about 50 to about 50 kGy.

20 In a further aspect of the present invention broadly there is provided a composite composition containing a cationic crosslinkable resin, a fiber reinforcement (optionally carbon fibers, aramid fibers, glass fibers or mats thereof) and an onium salt having an anion of the formula GaX_aR_b wherein X is a halogen atom or a hydroxy group, R is an aryl group, a and b are each represent an integer of 0 to 4 provided that the sum of a and b is 4.

25

In a still further aspect of the present invention broadly there is provided a method of preparing a composite, comprising exposing the composite composition of the present invention to an electron beam.

- 30 In a yet further aspect of the present invention broadly there is provided a photoresist composition comprising: a resin binder; and a photoactive component in an amount sufficient to permit development of an exposed coating layer of the composition, wherein the photoactive component is an onium gallate or gallates of organometallic complexes which are cationic initiators for polymerization. salt
35 having an anion of the formula GaX_aR_b wherein X is a halogen atom or a hydroxy group, R is an aryl group, a and b are each represent an integer of 0 to 4 provided that the sum of a and b is 4.

The photoresist composition of the present invention may be a negative-acting or positive-acting photoresist (in which case the resin may comprises an acid labile group).

- 5 Preferably the resin binder is a phenolic resin.

In a yet still further aspect of the present invention broadly there is provided an article of manufacture having at least one surface coated with the photoresist composition of the present invention. It will be appreciated that the surface of the
10 article may be entirely or partially coated (e.g. partially coated in a designated pattern thereon).

In another aspect of the present invention broadly there is provided method of forming a photoresist relief image on a substrate comprising applying a coating composition containing the photoresist composition of the present invention on a
15 substrate; and exposing the photoresist coating to a patterned activating radiation and developing the exposed photoresist layer to provide a relief image.

Preferably the activating energy (or radiation) is X-rays, gamma rays, and/or an
20 electron beam, more preferably an electron beam.

Preferably the substrate is a microelectronic wafer or a flat panel display substrate.

In order to illustrate the present invention, the following examples are provided. It is
25 understood that the Examples are not to be construed to limit the disclosed invention.

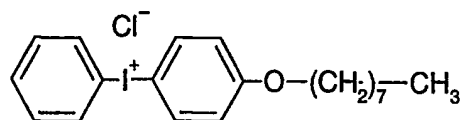
Reference Example 1 (Preparation of Lithium Tetrakis(pentafluorophenyl) gallate)

30 A 125 ml four-necked round bottom flask, equipped with a thermometer and two dropping funnels and a magnetic stirrer, is employed. The assembly was dried under an argon atmosphere. 80 ml of anhydrous pentene and 3.2 ml of bromopentafluorobenzene (25.67 mmol) were charged therein and then cooled to -78C. 10 ml of a 2.5M solution of n-butyllithium (25.04 mmol) in hexane were
35 added dropwise over one hour. The mixture was maintained under stirring for 3 to 5 hours at -78C. 10 ml of a solution of gallium chloride (6.25 mmol) in benzene (5.6g of GaCl₃ dissolved in 50 mL benzene under an argon atmosphere) were added dropwise to the mixture over one hour. The mixture was kept at -78C for 3

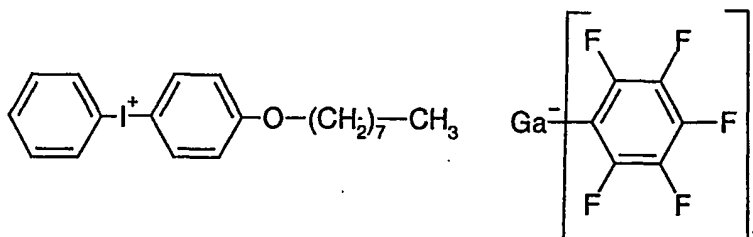
to 5 hours, then the cooling bath was removed. The reaction mixture was allowed to warm to ambient temperature as it was stirred overnight. The mixture was filtered, the filtrate was washed with hexane and then dried under reduced pressure at 60°C. A light yellow solid (containing LiCl) was obtained which has a melting point > 300°C. The product was characterized by ¹⁹F-NMR (DMSO).

Reference Example 2 (Preparation of Iodonium Tetrakis(pentafluorophenyl)gallate)

In a 50 ml round-bottom flask, Lithium Tetrakis(pentafluorophenyl) gallate prepared in accordance with Reference Example 1 is dissolved in 15 ml CH₂Cl₂. An equal molar amount of iodonium chloride having the formula:



in 15 ml CH₂Cl₂ was added dropwise with stirring at room temperature. The reaction mixture became cloudy. After stirring for two hours, the solvent was removed to yield a sticky residue. Chromatography on neutral alumina (a column of 3-5 cm in length was used) by elution with CH₂Cl₂ gave the iodonium tetrakis(pentafluorophenyl)gallate of the formula:

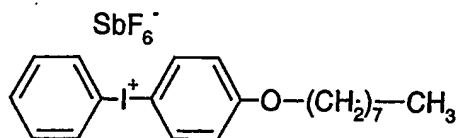


as a yellow sticky liquid. The yield was determined to be about 70 to about 85%. The structure was confirmed by ¹H-NMR and ¹⁹F-NMR.

Examples 1-6 and Comparative Examples 1-2

A portion of a batch of a bisphenol A epoxy resin (DER-332 manufactured by Dow Chemical) and having a molecular weight of about 340g/mole and an epoxy equivalent of about 170g, was divided into 8 aliquots. Each of the aliquots was blended with an amount of an initiator indicated in Table 1, to form the test samples. Initiator A is the initiator prepared in accordance with Reference Example 2 above. Initiator B is octyloxyphenylphenyliodonium

hexafluoroantimonate (OPPI) which is available from GE Silicones and has the formula:



The samples were heated to about 60 C for about 2 hours to dissolve the initiator
5 in the epoxy resin.

Table 1

Example No.	Initiator	Amount of initiator in sample wt. %
1	A	1.0
2	A	0.5
3	A	0.25
4	A	1.0
5	A	0.5
6	A	0.25
Comparative Ex. 1	B	1.0
Comparative Ex. 2	B	0.502

Each of the samples of the Examples is divided into separate sets and tested as follows:

- 10 A first set of samples were exposed to gamma radiation from a Cobalt 60 gamma radiation source to determine the temperature rise, the gel point and the energy needed to result in a 50% cure. The temperature rise is a measurement of the exothermicity of the reaction. The higher the temperature rise generally indicates an efficient polymerization reaction. The gel point is a measurement of the
- 15 minimum radiation dose needed to cure the composition. The results are shown in Table 2.

Table 2

Example No.	Temp. Rise °C	Gel Point (kGy)	50% Cure (kGy)
1	18	0.8	4.5
2	13	0.8	4.9
3	6	0.8	6.2
4	7	0.8	3.7
5	10	0.8	4.5
6	5	0.8	5.2
Comp. Ex. 1	10	0.9	4.3
Comp. Ex. 2	9	0.9	4.5

- A second set of the samples were subject to curing using an electron beam. The samples were cured for the purpose of dynamic mechanical analysis (DMA) tests.
- 5 The uncured samples were drawn into a syringe of about 1ml each. Next the samples were irradiated using a 1-10/1 electron accelerator. A 10 MeV pulsed electron beam was configured with a vertical horn to scan over a 30 cm wide path onto a variable speed conveyor belt. The instantaneous dose rate delivered during a pulse was 530 kGy per second. The dose deposited per pass under the beam
- 10 was 25 kGy per pass. A total dose of 150kGy absorbed the material was delivered by accumulating 6 successive passes under the beam. Each of the samples, once cured, are subjected to DMA testing. Results of the (DMA) tests are in Table 3.

Table 3

Example No.	Flexural Modulus (GPa)	Service Temperature	T _g °C (loss modulus)	T _g °C (tan δ)
1	2.50	150	190	207
2	2.30	160	195	212
3	2.43	158	180	207
4	2.33	158	190	207
5	2.45	160	193	210
6	2.02	160	185	212
Comp. Ex. 1	2.79	137	153	202
Comp. Ex. 2	2.81	100	108	135

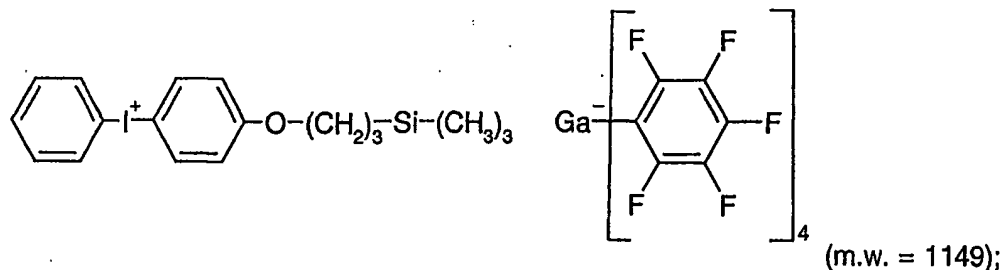
The flexural modulus was measured at room temperature after curing. The service temperature is the temperature in which modulus is one-half the modulus measured at 25°C. The T_g is the glass transition temperature of the cured resin, and is reported as a function of the loss modulus and as a function of the peak in the tan delta plot.

As can be seen in Table 3, the epoxy resin cured using an electron beam and the onium gallate of the present invention results in a cured resin having improved physical properties over the same resin cured with a conventional onium salt available in the art. Further, it can be seen that less of the initiator is need to cure the samples when the initiator of the present invention is used. These results suggest that the onium gallate of the present invention is very effective for curing cationic compositions as compare to another commercially available onium salt having the same cation.

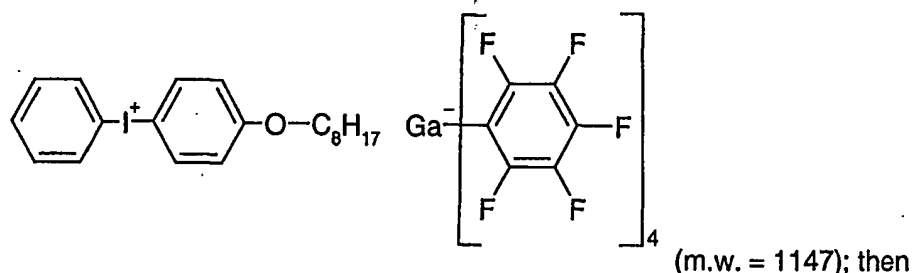
The foregoing description of the invention is merely illustrative thereof, and it is understood that variations and modifications can be made without departing from the scope or spirit of the invention as set forth in the following claims.

CLAIMS

1. A process for polymerizing or cross-linking a cationic polymerizable or cross-linkable component, said process comprising
- 5 a) forming a composition containing a component which is capable of cationic polymerizing or cationic cross-linking and an onium salt having an anion of the formula GaX_aR_b wherein X is a halogen atom or a hydroxy group, R is an aryl group or a substituted aryl group, a and b are each represent an integer of 0 to 4 provided that the sum of a and b is 4; and
- 10 b) exposing the composition to radiation selected from the group consisting of actinic radiation, X-rays, gamma-rays and an electron beam;
- with the proviso that when cross-linkable or polymerizable component is a matrix of the diglycidyl ether of bisphenol-A available commercially from Dow Chemical under the trademark DER 332; and the onium salt is present in an
- 15 amount of 1% by weight of the composition and is either:



or



the composition is exposed to radiation other than an electron beam at a beam voltage of 200mV and a dose of 10 Mrad.

2. A process for polymerizing or cross-linking a cationic polymerizable or cross-linkable component, said process comprising
- a) forming a composition containing a component which is capable of
- 25 cationic polymerizing or cationic cross-linking and an onium salt having an anion of

27.

the formula GaX_aR_b wherein X is a halogen atom or a hydroxy group, R is an aryl group or a substituted aryl group, a and b are each represent an integer of 0 to 4 provided that the sum of a and b is 4; and

5 b) exposing the composition to a dose of activating radiation to cross-link and/or polymerize the composition, such that the resultant composition has at least one of the following properties:

- i) a flexural modulus of less than about 2.5 Gpa;
- ii) a service temperature of greater than about 150°C;
- 10 iii) a T_g (measured as a function of the loss modulus) of greater than about 180°C; and/or
- iv) a T_g (measured as a function of the peak in a tan delta plot) of greater than about 207°C.

3. The process of claim 2, where the radiation is selected from the group
15 consisting of UV, actinic radiation, X-rays, gamma-rays and an electron beam.

4. The process of any preceding claim, where the onium salt contains a cation selected from the group consisting of iodonium, pyrylium, thiapyrylium, sulphonium, phosphonium, ferrocenium, and diazonium ions.
20

5. The process of claim 4, where the cation is an iodonium cation.

6. The process of claim 5, where the iodonium cation is a diaryliodonium cation.
25

7. The process of claim 6, where the diaryliodonium cation is 4-octyloxyphenylphenyl iodonium.

8. The process of any preceding claim, where the cation is a sulfonium cation.
30

9. The process of claim 9, where the sulfonium cation is selected from a triaryl sulfonium cation and/or a dialkylphenylacyl sulfonium cation.

10. The process of any preceding claim, where the anion is selected from the
35 group consisting of $[Ga(C_6F_5)_4]^-$, $[Ga(C_6H_4CF_3)_4]^-$, $[(C_6F_5)_2GaF_2]^-$, $[(C_6F_5)GaF_3]^-$, and $[Ga(C_6H_3F_2)_4]^-$.

11. The process of claim 10, where the anion is $[\text{Ga}(\text{C}_6\text{F}_5)_4]^-$.
12. The process of any preceding claim, where the onium salt is substantially dissolved in the polymerizable or cross-linkable component.
- 5 13. The process of any preceding claim, where the onium salt is added in an amount from about 0.25% to about 0.5% by weight of the composition.
- 10 14. The process of any preceding claim, where the composition is exposed to a radiation dose between about 0.8 and about 200 kGy.
- 15 15. The process of claim 14, where the dose is between about 50 and about 150 kGy.
16. The process of any preceding claim, where the radiation dose applied to produce a 50% cure of the composition is less than or equal to about 6.2 kGy.
17. The process of claim 16, where the radiation dose applied to produce a 50% cure is from about 4.5 kGy to about 6.2 kGy.
- 20 18. The process of any preceding claim, where minimum radiation dose required to initiate cure of the composition (gel point) is less than or equal to about 0.8 kGy.
- 25 19. The process of any preceding claim which comprises an exothermic reaction.
20. The process of claim 19, in which the reaction temperature rises by at least 5°C.
- 30 21. A composition obtained and/or obtainable by the process of any preceding claim which has at least one of the following properties:
- i) a flexural modulus of less than about 2.5 Gpa;
 - ii) a service temperature of greater than about 150°C;
 - 35 iii) a T_g (measured as a function of the loss modulus) of greater than about 180°C; and/or

iv) a T_g (measured as a function of the peak in a tan delta plot) of greater than about 207°C.

22. The composition of claim 21, which has at least one of the following properties:

- i) a flexural modulus of from about 2.0 to about 2.5 GPa;
- ii) a service temperature of from about 150°C to about 160°C;
- iii) a T_g (measured as a function of the loss modulus) of from about 180°C to about 195°C; and/or
- iv) a T_g (measured as a function of the peak in a tan delta plot) of from about 207°C to about 212°C.

23. A composite composition containing a cationically cross-linkable resin, a fiber reinforcement and an onium salt having an anion of the formula GaX_aR_b wherein X is a halogen atom or a hydroxy group, R is an aryl group, a and b are each represent an integer of 0 to 4 provided that the sum of a and b is 4.

24. The composite composition according to claim 23, where the fiber reinforcement is carbon fibers, aramid fibers, glass fibers or mats thereof.

25. A photo-resist composition comprising
a resin binder and
a photo-active component in an amount sufficient to permit development of an exposed coating layer of the composition, and where
the photo-active component is an onium gallate or gallates of organometallic complexes which are cationic initiators for polymerization, said salt having an anion of the formula GaX_aR_b wherein X is a halogen atom or a hydroxy group, R is an aryl group, a and b are each represent an integer of 0 to 4 provided that the sum of a and b is 4.

26. The photo-resist composition of claim 25, where the composition is a negative-acting photo-resist.

27. The photo-resist composition of claim 25, where the composition is a positive-acting photo-resist.

28. The photo-resist composition of any of claims 25 to 27, where the resin binder is a phenolic resin.
29. The photo-resist composition of any of claims 25 to 28, where the resin
5 comprises an acid labile group.
30. A method of preparing a composite, comprising exposing the composite composition of claim 23 or 24, to radiation selected from the group consisting of actinic radiation, UV, X-rays, gamma-rays and an electron beam.
10
31. A method of forming a photo-resist relief image on a substrate comprising applying the photo-resist composition of any of claims 25 to 29 on a substrate to form coating thereon ; and
15 exposing the photo-resist coating to a patterned activating radiation and developing the exposed photo-resist layer to provide a relief image.
32. The method of claim 31, wherein the activating energy is selected from the group consisting of actinic radiation, UV, X-rays, gamma-rays and an electron beam.
20
33. The method of claim 31 or 32, wherein the substrate is a micro-electronic wafer or a flat panel display.
34. An article of manufacture having at least one surface coated with the
25 composition of any of claims 21 to 29.
35. The article of claim 34, which is a micro-electronic wafer or a flat panel display.
- 30 36. Use of an onium salt as an initiator for cationic cross-linking and/or polymerization of a composition with activating radiation, where the onium salt has an anion of the formula GaX_aR_b wherein X is a halogen atom or a hydroxy group, R is an aryl group or a substituted aryl group, a and b are each represent an integer of 0 to 4 provided that the sum of a and b is 4;

the composition comprises a component which is capable of cationic polymerization and/or cross-linking to form after irradiation a cured composition having at least one of the following properties:

- i) a flexural modulus of less than about 2.5 GPa;
- 5 ii) a service temperature of greater than about 150°C;
- iii) a T_g (measured as a function of the loss modulus) of greater than about 180°C; and/or
- iv) a T_g (measured as a function of the peak in a tan delta plot) of greater than about 207°C.